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LOW-MELTING LEAD-FREE FLUXES FOR ENAMELS DEPOSITED ON GLASS

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Low-melting lead-free glass fluxes are developed to produce enamel for glass decoration. The glasses have the following parameters: CLTE $(82 - 85) \times 10^{-7} \text{ K}^{-1}$, chemical resistance to water less than 0.06%, and resistance to 2% solution of Na_2CO_3 less than 0.15%; fusibility 22 – 28 mm.

Among the most common industrial methods for glass decoration is applying lead-bearing enamel coatings, although their production and application is undesirable in view of the toxic effect of lead compounds (toxic materials of danger class 1, i.e., extremely dangerous) on human health [1, 2]. As a rule, the content of lead compounds at working places is 2 – 3 times higher than the maximum admissible concentration (MAC) (according to the new sanitary norms SanPin 11-19-94, the MAC of lead in working interiors should not be higher than 0.02 mg/m^3). The stricter requirements on environment safety stimulate the development of lead-free low-melting glasses to produce enamels for glass decoration.

In developing low-melting fluxes, the following boron-free enamel was taken as the base composition (here and elsewhere wt.%): 68 SiO_2 , 20 (TiO_2 , MgO , Al_2O_3 , BaO), 12 ($\text{Na}_2\text{O} + \text{K}_2\text{O}$). Its water resistance is classified as hydrolytic class II, with weight loss after 1 h exposure in hot (98°C) distilled water 0.18%; its CLTE is $107 \times 10^{-7} \text{ K}^{-1}$, and softening temperature of 550°C .

To lower the softening temperature and the CLTE, we have introduced oxides raising fusibility and at the same time decreasing the CLTE. We have studied the properties of four series of glasses containing:

Series I) 5, 10, 15, and 20% B_2O_3 and, accordingly, 63, 58, 53, 48% SiO_2 ; 12% ($\text{Na}_2\text{O} + \text{K}_2\text{O}$);

Series II) 43, 38, 33, 28, and 23% SiO_2 and, accordingly, 5, 10, 15, 20, 25% ZnO ; 12% ($\text{Na}_2\text{O} + \text{K}_2\text{O}$), 20% B_2O_3 ;

Series III) 2, 4, 6% Li_2O instead of Na_2O with 12% ($\text{Li}_2\text{O} + \text{Na}_2\text{O} + \text{K}_2\text{O}$) and a constant quantity of K_2O , 23% SiO_2 ; 20% B_2O_3 , 25% ZnO ;

Series IV) 19, 15, 11, and 7% SiO_2 and, accordingly, 4, 8, 12, 16% P_2O_5 ; 20% B_2O_3 , 25% ZnO , 12% ($\text{Li}_2\text{O} + \text{Na}_2\text{O} + \text{K}_2\text{O}$).

In each series the quantity of other components (TiO_2 , MgO , Al_2O_3 , BaO) remained constant.

Glasses were melted in an electric furnace in corundum crucibles at $1100 - 1200^\circ\text{C}$ with an exposure of 30 min.

The CLTE of glasses were determined in the temperature interval of $20 - 600^\circ\text{C}$, and the softening temperature of samples of height $50 \pm 2 \text{ mm}$ and diameter $4 \pm 1 \text{ mm}$ on a DKV-4 dilatometer at the heating rate of 2 K/min ; the chemical resistance was found by the granular method at 1 h exposure in hot (98°C) distilled water and in 2% solution of sodium carbonate of fraction $0.25 - 0.50 \text{ mm}$ [3], and the infrared absorption spectra in the range of $300 - 4000 \text{ cm}^{-1}$ were registered with a Perkin-Elmer 457 spectrophotometer. The fusibility and spreadability of glasses were determined based on the diameter of a drop formed in heating for 5 min at 800°C of a small bar of diameter 10 mm and height 8 mm molded from glass powder [4].

Boron compounds are good fluxes decreasing glass melting temperature. However, the effect of boron oxide is ambiguous: as the content of B_2O_3 in glasses of series I increases to 10%, their CLTE decreases from 107×10^{-7} to $92 \times 10^{-7} \text{ K}^{-1}$; with a higher content of B_2O_3 (10 – 20 %) it increases to $94 \times 10^{-7} \text{ K}^{-1}$. The softening temperature of glasses grows from 550 to 565°C while the B_2O_3 content increases to 10% and then decreases to 535°C with 10 – 20% B_2O_3 (Fig. 1).

The resistance of glass to chemical reactants grows as B_2O_3 content grows to 10%. A further replacement of silicon oxide by boron oxide from 10 to 20% in glasses of series I decreases their chemical resistance, i.e., increases the weight losses under treatment in hot water and 2% solution Na_2CO_3 (Fig. 1). The increase in B_2O_3 to 10% increases the spreadability of glass by 6 units and further increase from 10 to 20% decreases fusibility by 2 units; the maximum fluidity of the melt is registered at 10% B_2O_3 .

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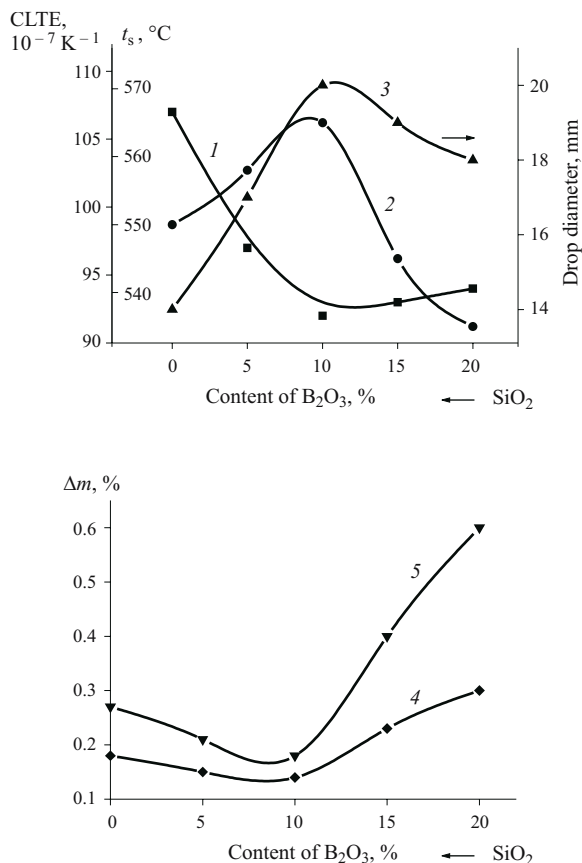


Fig. 1. Variations of CLTE, softening temperature t_s , fusibility, and chemical resistance of series I glasses versus B_2O_3 content: 1) CLTE; 2) t_s ; 3) fusibility; 4) weight loss Δm in hot (98°C) water; 5) the same in 2% solution of Na_2CO_3 .

Figure 2 shows the absorption spectra of the initial boron-free glass and synthesized glasses of series I and II. The spectrum of the boron-free glass has absorption bands with maxima at 1080, 780, 680, and 450 cm^{-1} [5] related to the Si–O bonds in the tetrahedrons $[\text{SiO}_4]$. When SiO_2 is replaced by B_2O_3 up to 10%, the glass spectra exhibit a decreased intensity of the absorption bands of groups $[\text{SiO}_4]$ and the shift of the main absorption band maximum to lower frequencies, from 1080 to 1050 cm^{-1} , which points to a decreased quantity of quartz groups and an increased number of groups $[\text{BO}_4]$. According to the data of A. A. Appen [6], under an excess of alkali, the boron ion acquires the oxygen ion from Na_2O and changes to coordination 4. Under a deficit of alkali, the increased concentration of B_2O_3 inevitably leads to the formation of triangles $[\text{BO}_3]$. The volume of the tetrahedron $[\text{BO}_4]$ is smaller than that of the tetrahedron $[\text{SiO}_2]$; therefore, replacing SiO_2 by B_2O_3 consolidates the glass structure, which is accompanied by a decreased CLTE and increased chemical resistance.

The spectra of glasses containing 15 and 20% B_2O_3 exhibit absorption bands with maxima at 1350 and 1230 cm^{-1} , which indicates the formation of groups $[\text{BO}_3]$ in glasses

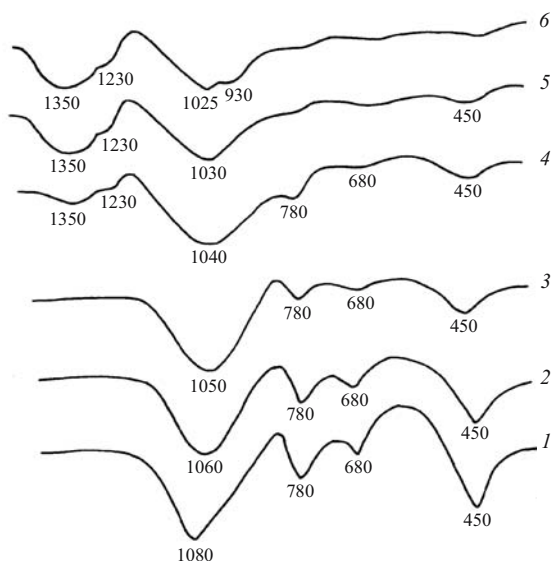


Fig. 2. IR spectra (cm^{-1}) of series I glasses: boron-free (1), glass with weight content of B_2O_3 equal to 5% (2), 10% (3), 15% (4), and 20% (5) and series II glass with weight content of B_2O_3 and ZnO equal to 20 and 25%, respectively (6).

[5, 6]. The intensity of the vibrations related to the Si–O bonds decreases. The spectrum of the glass bearing 20% boron anhydride exhibits a decreased intensity of the absorption band with the maximum at 1030 cm^{-1} and intensified absorption bands with peaks at 1230 and 1350 cm^{-1} , which is presumably caused by the transition of a part of $[\text{BO}_4]$ groups into $[\text{BO}_3]$ groups, which weakens the glass structure, increases its CLTE, and impairs its chemical resistance.

Consequently, groups $[\text{BO}_4]$ and $[\text{BO}_3]$ simultaneously coexist in glasses of series I and their concentration has a perceptible effect on the physicochemical properties of experimental glasses.

The CLTE of glasses of series II varies insignificantly on replacing SiO_2 by ZnO : $(92 - 94) \times 10^{-7} \text{ K}^{-1}$ and the softening temperature decreases from 535 to 507°C (Fig. 3). Zinc oxide facilitates glass melt spreading and has a favorable effect on its chemical resistance, i.e., its weight loss in hot water and in sodium carbonate solution decreases.

The spectrum of series II glass, which contains 25% ZnO and 20% B_2O_3 in addition to other components, has an additional adsorption band with a maximum at 930 cm^{-1} presumably determined by the formation of zinc-borate complexes (Fig. 2, curve 6) whose formation in the range of $900 - 1000 \text{ cm}^{-1}$ was also noted in [7].

The presence of lithium oxide has a favorable effect on the chemical resistance of glasses. Thus, replacing sodium oxide by lithium oxide in series III decreases weight loss in glasses treated with hot water and 2% sodium carbonate solution (Fig. 4). We also investigated the effect of lithium oxide on the fusibility of glasses. It initially grows and then consistently decreases. The maximum melt fluidity is observed

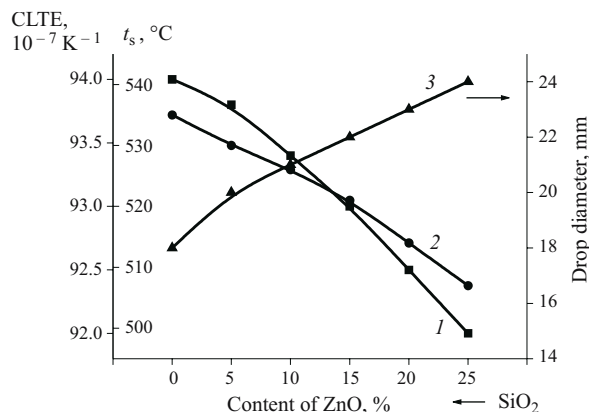


Fig. 3. Variation of CLTE, softening temperature t_s , fusibility, and chemical resistance of series II glasses versus ZnO content. Same notations as in Fig. 1.

with 3% content of Li₂O. The substitution of Li₂O for Na₂O in series III glasses decreases their CLTE from $92 \times 10^{-7} \text{ K}^{-1}$ to $88 \times 10^{-7} \text{ K}^{-1}$. The lithium ion has a smaller radius than the Na⁺ and K⁺ ions; therefore, it is more firmly bonded to the glass lattice and, thus decreases its CLTE [6]. The softening temperature of this series of glasses is 495–507°C.

It can be seen in Fig. 5 that when SiO₂ is replaced by P₂O₅ in glasses of series IV, their CLTE and sintering temperature decrease to $82.0 \times 10^{-7} \text{ K}^{-1}$ and 478°C, respectively, whereas their spreadability increases.

The chemical resistance of glasses is significant for estimating the service properties of glasses. The resistance of series IV glasses to chemical reactants increases as the content of P₂O₅ grows from 4 to 16%. It should be noted that this series of glasses suffers small losses when treated by hot water (0.02–0.06%) or by 2% Na₂CO₃ solution (less than 0.15%).

The properties of experimental glasses of series IV, that is the CLTE ($82–85 \times 10^{-7} \text{ K}^{-1}$), softening temperature 478–480°C, chemical resistance to water less than 0.06% and to 2% solution of Na₂CO₃ less than 0.15%, and spreadability 22–28 mm make them the most suitable for producing enamels for glass decoration.

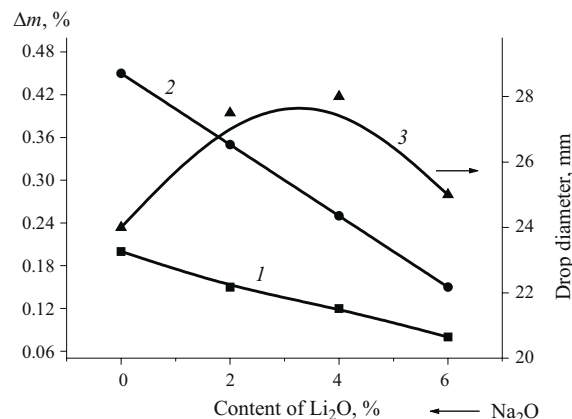


Fig. 4. Variation of chemical resistance and fusibility of series III glasses versus Li₂O substituted for Na₂O: 1) weight loss Δm in hot (98°C) water; 2) the same in 2% solution of Na₂CO₃; 3) fusibility.

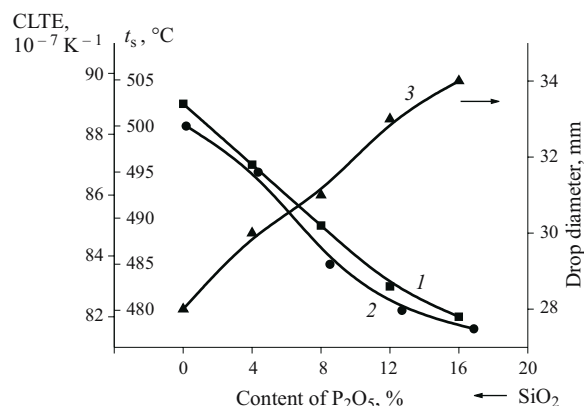


Fig. 5. Variation of CLTE (1), softening temperature t_s (2), and fusibility (3) of series IV glasses versus P₂O₅ content.

Thus, it is possible to synthesize low-melting nontoxic chemically resistant glasses in the considered composition range.

REFERENCES

1. V. M. Ivanova and G. V. Kochetkova, *Treatment of Glass Articles Using Silicate Paints* [in Russian], VNIIESM, Moscow (1978).
2. A. G. Lantsetti and M. L. Nesterenko, *Production of Fancy Glass* [in Russian], Vysshaya Shkola, Moscow (1972).
3. N. M. Pavlushkin, G. G. Sentyurin, and R. Ya. Khodakovskaya, *Practical Course in Glass and Glass Ceramics Technology* [in Russian], Stroiizdat, Moscow (1970).
4. G. I. Belyaev and Ya. I. Belyi, "The effect of fluorine on properties of low-melting enamels," *Steklo Keram.*, No. 4, 34–36 (1965).
5. I. I. Plyuskina, *Infrared Spectra of Silicates* [in Russian], Nauka, Moscow (1967).
6. A. A. Appen, *Chemistry of Glass* [in Russian], Khimiya, Leningrad (1970).
7. P. Smith, S. Garcia-Blanco, and L. Rivoir, "A new structural type of metaborate anion," *Z. Kristallogr.*, **115**(5–6), 460–463 (1961).